ATTACHMENT I

TRACEABILITY PROTOCOL FOR ESTABLISHING TRUE CONCENTRATIONS OF GASES USED FOR CALIBRATION AND AUDITS OF CONTINUOUS SOURCE EMISSION MONITORS

(Protocol No. 1)

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4.0 TRACEABILITY PROTOCOL FOR ESTABLISHING TRUE CONCENTRATION OF GASES USED FOR CALIBRATION AND AUDITS OF CONTINUOUS SOURCE EMISSION MONITORS (PROTOCOL NO. 1)

Performance standards promulgated[1,2,3] by the U.S. Environmental Protection Agency for stationary sources require the installation and operation of continuous monitoring systems for specified pollutants. Extractive continuous monitoring systems for gaseous pollutants must be calibrated and audited using gas standards that are accurate and stable.

The traceability procedure described here is intended to minimize systematic and random errors during the analysis of calibration and audit gas standards and to establish the true concentrations by means of National Bureau of Standards, Standard Reference Materials (NBS, SRM). The procedure provides for a direct comparison between the calibration and audit gas standards and an NBS, SRM or a gas manufacturer's primary standard (GMPS) which is referenced to NBS, SRM. All comparisons are made using instruments calibrated with applicable NBS, SRM. Traceability must be performed by the gas standard manufacturer at the time of purchase. Reanalysis as described in 4.1.5 may be performed by the gas standard manufacturer or by the user.

This procedure is applicable to any continuous, semi-continuous, or periodic analysis instrument that meets the performance requirements in the following sections.

4.1 Establishing Traceability of Commercial Cylinder Gases to NBS,SRM Cylinder Gases

4.1.1 Procedure for Instrument Calibration - The following procedures for periodic span checks are prescribed to minimize systematic error. Separate procedures for instrument span checks are described for linear and nonlinear instruments. For this purpose, a linear instrument is defined as one which yields a calibration curve that deviates by 2% or less of full scale from a straight line drawn from the point determined by zero gas to the highest calibration point. To be considered linear, the ifference between the concentrations indicated by the calibration curve and the straight line must not exceed 2% of full scale at any point on the curve.

4.1.1.1 Instrument Multipoint Calibration - A multipoint calibration curve is prepared monthly using two SRM cylinder gases and zero gas. The zero gas must not contain more than 0.2% of the full scale concentration of the component being analyzed. In addition, zero gas must be free of any impurity that will give a response on the analytical instrument. A list of SRM cylinder gases recommended for traceability of commercial cylinder gases is given in Table 4.1. A list of new stationary sources that are required to install continuous source emission monitors for gaseous pollutants and diluent gases (O_2 and CO_2) is given in Table 4.2. This table also lists existing stationary sources that may be required to install continuous source emission monitors for gaseous pollutants and diluent gases.

The multipoint calibration is accomplished by diluting the highest SRM with zero gas using a calibration flow system. Obtain the instrument response for six points representing 0, 10, 30, 50, 75, and 100% of the instrument full scale. Plot the data and construct the calibration curve. Obtain the instrument response for the other lower SRM without dilution. Compare the apparent concentrations from the calibration curve with the true concentration of the lower SRM. If the difference between the apparent concentration and the true concentration of the lower SRM exceeds 3% of the true concentration, repeat the multipoint calibration procedure. Test the calibration curve for linearity as defined in 4.1.1 and proceed to either 4.1.1.2 or 4.1.1.3.

4.1.1.2 Instrument Span Check for Linear Response

Instrument - At the start of each day that cylinder gases are to be analyzed, check instrument response to the highest SRM (or GMPS) in the range to be used and to zero gas. Adjust response to the value obtained in the most recent multipoint calibration and proceed to 4.1.2. Cylinder gases analyzed with a linear instrument must not have a concentration greater than 15% above the highest available SRM concentration.

Table 4.1. NBS, SRM AVAILABLE FOR TRACEABILITY OF CALIBRATION AND AUDIT GAS STANDARDS

Cylinder Gases

SRM	Type	Size liters at STP	Nominal Concentrations
(1)	Sulfur Dioxide in N_2	870	50 ppm
(1)	Sulfur Dioxide in N_2	870	90 ppm
1661	Sulfur Dioxide in N_2	870	500 ppm
1662	Sulfur Dioxide in N_2	870	1000 ppm
1663	Sulfur Dioxide in N_2	870	1500 ppm
1664	Sulfur Dioxide in N_2	870	2500 ppm
(2)	Sulfur Dioxide in N_2	870	3500 ppm
1684	Nitric Oxide in N_2	870	100 ppm
1685	Nitric Oxide in N_2	870	250 ppm
1686	Nitric Oxide in N_2	870	500 ppm
1687	Nitric Oxide in N_2	870	1000 ppm
2630	Nitric Oxide in N_2	870	1500 ppm
2631	Nitric Oxide in N_2	870	3000 ppm
(3)	Nitrogen Dioxide in Air	870	250 ppm
(3)	Nitrogen Dioxide in Air	870	500 ppm
(3)	Nitrogen Dioxide in Air	870	1000 ppm
(3)	Nitrogen Dioxide in Air	870	2500 ppm
(3)	Oxygen in N_2	870	2%
(3)	Oxygen in N_2	870	10%
1609	Oxygen in N_2	870	21%

(continued)

Table 4.1. (continued)

SRM	Type	Size liters at STP	Nominal Concentrations
2622	Carbon Dioxide in N_2	870	2%
2626	Carbon Dioxide in N_2	870	4%
1674	Carbon Dioxide in N_2	870	7%
1675	Carbon Dioxide in N_2	870	14%

(1) SRM currently under development, planned issue date March 1980.

(2) SRM currently under development, planned issue date October 1980.

(3) SRM currently under development, planned issue date December 1979.

Table 4.2. CONTINUOUS SOURCE EMISSION MONITORS FOR NEW AND EXISTING STATIONARY SOURCES

Pollutant	Source	EPA Regulation	Monitors Mid-Range and Span Gas Concentrations, ppm (3)
SO_2	Steam Generation	SPNSS (1)	Oil-500, 900; Coal-750, 1350
	Steam Generation	SIP (2)	Coal-500 to 2000 (4)
	Petro. Refinery	SPNSS	50, 90
	Sulfuric Acid Plant	SPNSS	500, 900
	Sulfuric Acid Plant	SIP	2000 to 3500 (4)
	Primary Smelters: Copper, Lead & Zinc	SPNSS	1600 to 1800
NO	Steam Generation	SPNSS	Gas & Oil - 250, 450
			Coal - 500, 900
	Steam Generation	SIP	Coal - 400 to 1500 (4)
NO_2	Nitric Acid Plant	SPNSS	250, 450
	Nitric Acid Plant	SIP	200 to 1000 (4)
O_2	Steam Generation	SPNSS	EPA Regulation 40 CFR 60 (SPNSS) does not require a specific setting for monitor full scale
CO_2	Steam Generation	SPNSS	

(1) Standards of Performance for New Stationary Sources.

(2) State Implementation Plans (for existing stationary sources).

(3) Required setting for monitor full scale (called span value) is specified in SNPSS (40 CFR 60). Span is 90% and mid-range is 50% of the monitor full scale.

(4) This is the range of typical operation. Mid-range and span gas concentrations needed will depend on state regulations. However, the concentrations should be within the range shown.

4.1.1.3 Instrument Span Check for Nonlinear Response Instrument - At the start of each day that cylinder gases are to be analyzed, check instrument response to two SRM (or GMPS) in the range of calibration gases to be analyzed and to zero gas as follows. First, set the instrument zero with zero gas and then adjust the instrument response to the highest SRM (or GMPS) to the value obtained in the most recent multipoint calibration. Next, obtain the response to the lower SRM (or GMPS). If the response to the lower SRM (or GMPS) varies by more than 3% from the response obtained in the most recent multipoint calibration, a full multipoint calibration must be performed as in 4.1.1.1; otherwise proceed to 4.1.2. Calibration gases analyzed with a nonlinear instrument must not have a concentration greater than the highest available SRM concentration.

4.1.2 Procedure for Analysis of Cylinder Gas for True Concentration - The following procedure is designed to establish the true concentration of a cylinder gas. The procedure involves the direct comparison of the cylinder gas with the SRM (or GMPS) and compensates for variations in instrument response between the time of daily span check and the time of analysis. Significant variations in response often result from changes in room temperature, line voltage, etc. The procedure is as follows:

1. After the gas cylinder has been filled, a minimum 4-day holding time must be observed before the following protocol analysis is initiated. (Note: when steel cylinders are used for SO_2, a minimum 15 day holding time must be observed before the following protocol analysis is initiated.)

2. Analyze each cylinder gas directly against the nearest SRM (or GMPS) by alternate analyses of the SRM and cylinder gas in triplicate (three pairs). Adjust the instrument span if necessary prior to the analysis but do not adjust the instrument during the triplicate analyses. The response to zero gas shall be obtained with sufficient frequency that the change in successive zero responses does not exceed 1% of full scale.

3. For each of the six analyses, determine the apparent concentration of the SRM (or GMPS) or cylinder gas from the calibration curve.

4. For each pair of analyses, one SRM (or GMPS) and one cylinder gas, calculate the true concentration of the cylinder gas by:

$$\text{True Conc. of Cyl. Gas} = \text{Apparent Conc. of Cyl. Gas} \times \frac{\text{True Conc. of SRM (or GMPS)}}{\text{Apparent Conc. of SRM (or GMPS)}}$$

5. Determine the mean of the three values for true concentration of the cylinder gas.

6. If any one of the three values differs from the mean of the three values by greater than 1.5%, discard the data, reset the instrument span if necessary, and repeat steps 1-4.

4.1.3 Use of Manufacturer's Primary Standards - Gas manufacturer's primary standards (GMPS) are gas mixtures prepared in pressurized containers and analyzed against SRM cylinder gases. Their purpose is to conserve SRM where large quantities of gas cylinders are analyzed. GMPS may be substituted for SRM for instrument span check in 4.1.1.2 and 4.1.1.3, and for cylinder gas analysis in 4.1.2 if the following conditions are met. In no case may GMPS be substituted for SRM for the required instrument multipoint calibrations in 4.1.1.1.

1. GMPS must have been analyzed against SRM cylinder gases as described in 4.1.1 and 4.1.2 within 30 days of their use for cylinder gas analysis. It is preferred that GMPS be analyzed on the days that instrument multipoint calibrations are performed.

2. GMPS must not have changed in concentration by more than 1% per month (average) for the 3-month period prior to their use for cylinder gas analysis.

4.1.4 <u>Verification of Cylinder Gas Stability</u> - The stability of reactive gases (including cylinder gas of sulfur dioxide, nitric oxide, and nitrogen dioxide) must be verified before use. The stability of each cylinder gas is verified by performing a second set of triplicate analyses (using procedure in 4.1.2) a minimum of 7 days after the first set of triplicate analyses. The mean of the second triplicate analyses must not differ from the mean of the first triplicate analysis by more than 1.5%.

4.1.5 <u>Reanalysis of Cylinder Gases</u> - Reanalysis of reactive gases by the gas manufacturer or user must be performed every 6 months from the last analysis date by the procedure in 4.1.2. Cylinder gases used for audits may need to be analyzed more frequently than every 6 months. Reanalysis of diluent gases (O_2 and CO_2) by the gas manufacturer or user must be performed every 12 months from the last analysis date by the procedure in 4.1.2.

4.1.6 <u>Minimum Cylinder Pressure</u> - No cylinder gas should be used below a cylinder pressure of 200 psi as shown by the cylinder gas regulator.

4.1.7 <u>Cylinder Label and Analysis Report</u> - Each gas cylinder shipped by a gas manufacturer to a user must contain the following minimum traceability information on a gummed label affixed to the cylinder wall and/or a tag attached to the cylinder valve:

1. Cylinder number
2. Mean concentration of cylinder gas, ppm or mol% (on last analysis date)
3. Balance gas used
4. Last analysis date
5. Expiration date (six months after the last analysis date for reactive gases and 12 months for diluent gases).

In addition, a written analysis report should be prepared which certifies that the cylinder gas has been analyzed according to this protocol. The analysis report should contain the following information:

1. Cylinder number

2. Mean concentration of cylinder gas, ppm or mol% (on last analysis date)

3. Replicate analysis data

4. Balance gas used

5. NBS,SRM numbers used as primary standards

6. Analytical principle used

7. Last analysis date.

The user should maintain a file of all analysis reports for three years.

4.2 Performance Audit Program

With the initiation and use of this traceability protocol, the U.S. Environmental Protection Agency will initiate a national performance audit program of cylinder gas prepared by this protocol. Cylinder gas prepared following the protocol will be obtained directly or indirectly by the U.S. Environmental Protection Agency and analyzed in its laboratory for accuracy compared with the gas manufacturer's reported concentration.

4.3 References

1. Requirements for Submittal of Implementation Plans and Standards for New Stationary Sources - Emission Monitoring. Federal Register 40, Number 194, October 6, 1975, pages 46240-46270.

2. Part 60 - Standards of Performance for New Stationary Sources - Emission Monitoring Requirements and Revisions to Performance Testing Methods, Federal Register 40, Number 246, December 22, 1975, pages 59204 and 59205.

3. Part 60 - Standards of Performance for New Stationary Sources - Primary Copper, Zinc and Lead Smelters, Federal Register 40, Number 10, January 15, 1976, pages 2332-2341.

6.3.2 Response Time Test Procedure. At a minimum, each response time test shall provide a check of the entire sample transport line (if applicable), any sample conditioning equipment (if applicable), the pollutant analyzer, and the data recorder. For in-situ systems, perform the response time check by introducing the calibration gases at the sample interface (if applicable), or by introducing the calibration gas cells or filters at an appropriate location in the pollutant analyzer. For extractive monitors, introduce the calibration gas at the sample probe inlet in the stack or at the point of connection between the rigid sample probe and the sample transport line. If an extractive analyzer is used to monitor the effluent from more than one source, perform the response time test for each sample interface.

To begin the response time test, introduce zero gas (or zero cell or filter) into the continuous monitor. When the system output has stabilized, switch to monitor the stack effluent and wait until a "stable value" has been reached. Record the upscale response time. Then, introduce the high-level calibration gas (or gas cell or filter). Once the system has stabilized at the high-level concentration, switch to monitor the stack effluent and wait until a "stable value" is reached. Record the downscale response time. A "stable value" is equivalent to a change of less than 1 percent of span value for 30 seconds or 5 percent of measured average concentration for 2 minutes. Repeat the entire procedure three times. Record the results of each test on a data sheet (example is shown in Figure 2-5). Determine the means of the upscale and downscale response times using Equation 2-1. Report the slower time as the system response time.

6.3.3 Field Test for Zero Drift and Calibration Drift. Perform the zero and calibration drift tests for each pollutant analyzer and data recorder in the continuous monitoring system.

6.3.3.1 Two-hour Drift. Introduce consecutively zero gas (or zero cell or filter) and high-level calibration gas (or gas cell or filter) at 2-hour intervals until 15 sets (before and after) of data are obtained. Do not make any zero or calibration adjustments during this time unless otherwise prescribed by the manufacturer. Determine and record the amount that the output had drifted from the recorder zero and high-level value on a data sheet (example is shown in Figure 2-6). The 2-hour periods over which the measurements are conducted need not be consecutive, but must not overlap. Calculate the zero and calibration drifts for each set. Then calculate the mean, confidence interval, and zero and calibration drifts (2-hour) using Equations 2-1, 2-2, and 2-3. In Equation 2-3, use the span value for R.V.

6.3.3.2 Twenty-Four Hour Drift. In addition to the 2-hour drift tests, perform a series of seven 24-hour drift tests as follows: At the beginning of each 24-hour period, calibrate the monitor, using mid-level value. Then introduce the high-level calibration gas (or gas cell or filter) to obtain the initial reference value. At the end of the 24-hour period, introduce consecutively zero gas (or gas cell or filter) and high-level calibration gas (or gas cell or filter); do not make any adjustments at this time. Determine and record the amount of drift from the recorder zero and high-level value on a data sheet (example is shown in Figure 2-7). Calculate the zero and calibration drifts for each set. Then calculate the mean, confidence interval, and zero and calibration drifts (24-hour) using Equations 2-1, 2-2, and 2-3. In Equation 2-3, use the span value for R.V.

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